

An Additivity Rule for the Vapor Pressure Lowering of Aqueous Solutions

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The question is discussed whether, and to what extent, the vapor pressure lowering of an aqueous solution containing two salts A and B can be compounded additively from the vapor pressure lowerings of a solution containing the salt A alone and another solution containing the salt B alone. In some instances the additivity of vapor pressure lowering is true within less than 0.5 percent; six systems have been examined and the greatest deviation from additivity amounts to 2.0 percent.

1. Introduction

It has been shown [1]¹ that in some instances the vapor pressure lowering of a solution of two salts is approximately an additive effect of the vapor pressure lowering due to each salt separately. If this could be established, vapor pressure data for many three-component systems containing water and two salts could be calculated from known data for aqueous solutions of single salts. Moreover, related properties of aqueous solutions of two salts, such as osmotic pressure, freezing point depression, boiling point elevation, could also be calculated. The rule, even if only approximately true, could have many practical applications.

The additivity rule can be illustrated as follows. In a study of the system water-sodium chloride-barium chloride [2] it was found that at 25 °C a solution 1.0073 m with respect to sodium chloride and 1.0448 m with respect to barium chloride was in vapor phase equilibrium with a solution containing sodium chloride only at a concentration 2.6185 m. The vapor pressure lowerings of solutions of sodium chloride at 25 °C have been tabulated [3] and it can be shown that a solution 2.6185 m in sodium chloride has a vapor pressure 2.181 mm Hg lower than that of pure water at the same temperature. The vapor pressure lowering of the mixed solution of sodium chloride and barium chloride must be the same, 2.181 mm Hg.

There are many ways by which we could attempt to predict this vapor pressure lowering. We could assume that the lowering was the sum of that due to a solution containing sodium chloride only at a con-

centration of 1.0073 m and that due to a solution of barium chloride only at a concentration of 1.0448 m. Since the vapor pressure lowering of the sodium chloride solution is 0.7929 mm Hg and that of the barium chloride solution is 1.232 mm Hg, the predicted value for the mixed solution is 2.025 mm Hg, which is not in good agreement with the observed value.

We might use relative molal vapor pressure lowering at total ionic concentrations equal to that of the mixed solution. The total ionic concentration of the mixed solution is $1.0073 + 1.5 \times 1.0448 = 2.5755$. At this concentration the relative molal vapor pressure lowering, $(p^\circ - p)/(mp^\circ)$, of a sodium chloride solution is 0.03500 and hence the predicted contribution of sodium chloride is 0.8374 mm Hg. Similarly, the relative molal vapor pressure lowering of a barium chloride solution at this total ionic concentration is 0.05421, so that the predicted contribution of barium chloride is 1.343 mm Hg, the total contribution being 2.282 mm Hg. Again, this does not agree well with the observed value.

A third possibility is to compare solutions of the same total ionic strength. The total ionic strength of the mixed solution is 4.1417; a solution containing sodium chloride only at this total ionic strength is 4.1417 m. Its relative molal vapor pressure lowering, $(p^\circ - p)/(mp^\circ)$, at this total ionic strength is 0.03734 and the vapor pressure lowering per mole of salt, $(p^\circ - p)$, is 0.8869 mm Hg. The additivity rule requires that we use the vapor pressure lowering per mole of salt at the total ionic strength of the mixed solution. Hence the contribution to the vapor pressure lowering due to the 1.0073 moles of sodium chloride is 0.8934 mm Hg. A solution containing barium chloride only at a total ionic strength of 4.1417 is 1.3806 m in concentration. The vapor pressure lowering per mole of barium chloride at this concentration is 1.234 mm Hg or 1.289 mm Hg for

¹ Figures in brackets indicate the literature references at the end of this paper.

the 1.0448 moles of barium chloride in the mixed solution. If the vapor pressure lowering of the mixed solution is truly additive, a lowering of 2.182 mm Hg is predicted, which compares very well with the observed value of 2.181 mm Hg.

It is the purpose of this paper to consider data for this salt pair at other concentrations and data for other systems, especially those containing an alkali metal chloride and an alkaline earth metal chloride.

2. Vapor Pressure Lowerings of Single Salt Solutions

Values of the relative molal vapor pressure lowerings, $(p^\circ - p)/(mp^\circ)$ of both sodium chloride and potassium chloride solutions have been tabulated [3]. It will be convenient to tabulate similar data for solutions of calcium chloride and of barium chloride. The osmotic coefficients of solutions of barium chloride are known [2]; they are related to the vapor pressure of the solution by the expression:

$$-3m\varphi = 55.51 \ln (p/p^\circ)$$

and, therefore values of $(p^\circ - p)/(mp^\circ)$ can be calculated. They are given in table 1. Values for calcium chloride solutions can be calculated from osmotic coefficient data for this salt [3]; they are also given in table 1.

TABLE 1. *Relative molal vapor pressure lowering of solutions of calcium chloride and of barium chloride at 25 °C*

<i>m</i>	$(p^\circ - p)/(mp^\circ)$	
	Ca Cl ₂	Ba Cl ₂
0.1	0.04605	0.04541
.2	.04637	.04510
.3	.04701	.04530
.4	.04793	.04570
.5	.04894	.04619
.6	.05001	.04676
.7	.05113	.04736
.8	.05232	.04800
.9	.05363	.04866
1.0	.05504	.04933
1.1	.05637	.05002
1.2	.05773	.05071
1.3	.05914	.05141
1.4	.06056	.05210
1.5	.06198	.05278
1.6	.06340	.05346
1.7	.06481	.05411
1.8	.06623	.05475
1.9	.06767	.05536
2.0	.06910	.05593

3. Solutions of Sodium Chloride and Potassium Chloride at 25 °C

The vapor pressures of a number of solutions containing both sodium chloride and potassium chloride have been determined [4]. Some of these data are used to study the additivity rule; the results are given in table 2. The first column gives the molality M_{NaCl} of a solution containing sodium chloride only, in isopiestic (vapor phase) equilibrium with a

solution of potassium chloride and sodium chloride with molalities given in the second and third columns. The fourth column gives the vapor pressure lowering observed in this isopiestic experiment and the fifth column that calculated by the additivity rule. The last column gives the percentage difference between the observed and calculated vapor pressure lowerings.

TABLE 2. *Vapor pressure lowerings of solutions of sodium chloride and potassium chloride at 25 °C*

M_{NaCl}	m_{KCl}	m_{NaCl}	$(p^\circ - p)$ mm Hg		Δ^a
			obs.	calc.	
0.5012	0.3099	0.1995	0.3917	0.3923	0.2
1.0493	.5177	.5571	.8268	.8300	.6
1.6223	.8581	.8244	1.299	1.309	.8
2.3248	.9701	1.4490	1.913	1.933	1.1
3.3188	1.5328	1.9780	2.845	2.884	1.4
4.0043	2.1391	2.1700	3.532	3.592	1.7
4.4461	3.1963	1.7241	3.994	4.066	1.8
4.6857	1.6005	3.3522	4.247	4.318	1.7

^a Δ is the percentage difference between observed and calculated vapor pressure lowerings.

4. Solutions of an Alkali Metal Chloride and Alkaline Earth Metal Chloride at 25 °C

Tables 3 through 6 give similar data for the following salt pairs:

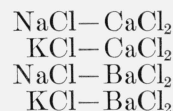


TABLE 3. *Vapor pressure lowerings of solutions of sodium chloride and calcium chloride at 25 °C*

M_{NaCl}	m_{NaCl}	m_{CaCl_2}	$(p^\circ - p)$ mm Hg		Δ^a
			obs.	calc.	
0.5339	0.2495	0.1968	0.4173	0.4150	0.6
1.0420	.4375	.3929	.8207	.8109	1.2
1.5186	.5078	.6248	1.211	1.194	1.4
2.7546	1.2728	.8300	2.307	2.265	2.0
3.4285	1.2284	1.1858	2.952	2.902	1.7
4.5821	2.1539	1.2356	4.137	4.047	2.2
5.4851	3.8795	0.7894	5.124	5.036	1.7

^a Δ is the percentage difference between observed and calculated vapor pressure lowerings.

TABLE 4. *Vapor pressure lowerings of solutions of potassium chloride and calcium chloride at 25 °C*

M_{KCl}	m_{KCl}	m_{CaCl_2}	$(p^\circ - p)$ mm Hg		Δ^a
			obs.	calc.	
1.5135	0.9350	0.3559	1.141	1.135	0.5
1.5240	.7744	.4569	1.149	1.143	.5
2.7872	1.9415	.4654	2.121	2.110	.5
2.7986	1.4805	.7194	2.130	2.126	.2
2.7986	1.0515	.9406	2.130	2.128	.1

^a Δ is the percentage difference between observed and calculated vapor pressure lowerings.

TABLE 5. Vapor pressure lowerings of solutions of sodium chloride and barium chloride at 25 °C

M_{NaCl}	m_{NaCl}	m_{BaCl_2}	(p°-p) mm Hg		Δ^a
			obs.	calc.	
0.5044	0.2213	0.2037	0.3941	0.3926	0.4
1.2328	.6389	.4092	.9746	.9722	.2
1.5683	.2721	.8790	1.253	1.255	.2
2.0021	1.0496	.6303	1.626	1.622	.2
2.3615	1.1799	.7744	1.946	1.948	.1
2.7147	1.3969	.8514	2.270	2.272	.1
2.7147	0.6356	1.3458	2.270	2.276	.3

^a Δ is the percentage difference between observed and calculated vapor pressure lowerings.

TABLE 6. Vapor pressure lowerings of solutions of potassium chloride and barium chloride at 25 °C

M_{KCl}	m_{KCl}	m_{BaCl_2}	(p°-p) mm Hg		Δ^a
			obs.	calc.	
0.7899	0.4185	0.2603	0.5987	0.5982	0.1
1.0743	.5648	.3514	.8112	.8133	.3
1.5519	.2358	.8588	1.170	1.177	.6
2.2466	.8579	.8894	1.701	1.725	1.4
2.7188	.5746	1.3145	2.068	2.095	1.3
2.7763	1.5011	0.8090	2.112	2.055	2.0
2.8600	.9462	1.1832	2.178	2.216	1.7

^a Δ is the percentage difference between observed and calculated vapor pressure lowerings.

In each table the first column gives the molality of the single salt solution (sodium chloride or potassium chloride) in isopiestic equilibrium with the solution containing two salts at molalities given in the third and fourth columns. The next two columns give observed and calculated values of the vapor pressure lowering and the last column the percentage difference between observed and calculated values.

The data for the sodium chloride-barium chloride system are taken from a previous publication [2]; the data for the other systems are new.

5. System Containing Three Solutes

A few measurements have been made on the four component system water-sodium chloride-potassium chloride-barium chloride, with the results given in table 7.

TABLE 7. Vapor pressure lowerings of solutions of sodium chloride, potassium chloride, and barium chloride at 25 °C

M_{NaCl}	m_{NaCl}	m_{KCl}	m_{BaCl_2}	(p°-p) mm Hg		Δ^a
				obs.	calc.	
1.4218	0.4708	0.4708	0.3559	1.130	1.139	0.8
1.4174	.3110	.3110	.5654	1.126	1.134	.7
1.4174	.1740	.1740	.7449	1.126	1.133	.6
1.4174	.1127	.1127	.8250	1.126	1.133	.6
2.5903	1.1980	1.1980	.2126	2.155	2.177	1.0
2.5903	1.0281	1.0281	.4292	2.155	2.180	1.2
2.5567	0.5509	0.5509	1.0022	2.124	2.148	1.1
2.5567	.3521	.3521	1.2443	2.124	2.145	1.0

^a Δ is the percentage difference between observed and calculated vapor pressure lowerings.

6. Summary

The validity of the additivity rule can be appreciated by considering the percentage difference between observed and calculated vapor pressure lowerings and especially the upper and lower limits of these percentage differences for each system. These are as follows:

	%
NaCl-KCl	0.2-1.8
NaCl-CaCl ₂	.6-2.2
KCl-CaCl ₂	.1-0.5
NaCl-BaCl ₂	.1-0.4
KCl-BaCl ₂	.1-2.0
NaCl-KCl-BaCl ₂	.6-1.2

The agreement is very good in some instances, for example, the potassium chloride-calcium chloride system and the sodium chloride-barium chloride system. Even in the worst case the difference is only 2 percent. This is not tolerable in an investigation of the more detailed interactions of multi-component salt solutions. It may, however, be of sufficient accuracy in other applications; a decision can only be made with the object of an application of this additivity rule in mind.

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7. References

- [1] R. A. Robinson and R. H. Stokes, *Trans. Faraday Soc.* **41**, 752 (1945).
- [2] R. A. Robinson and V. E. Bower, *J. Res. NBS* 69A (Phys and Chem) No. 1, 19-27 (1965).
- [3] R. A. Robinson and R. H. Stokes, *Electrolyte solutions*, appendix 8.3, 2d. ed. (Butterworths Scientific Publications, London, 1959).
- [4] R. A. Robinson, *J. Phys. Chem.* **65**, 662 (1961)